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Cluster Approach to the Electronic Properties Modeling of Nanocrystal Structures

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Cluster approach to the electronic properties modeling of nanocrystal structures

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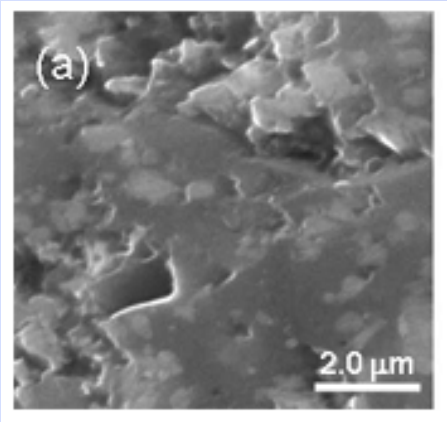
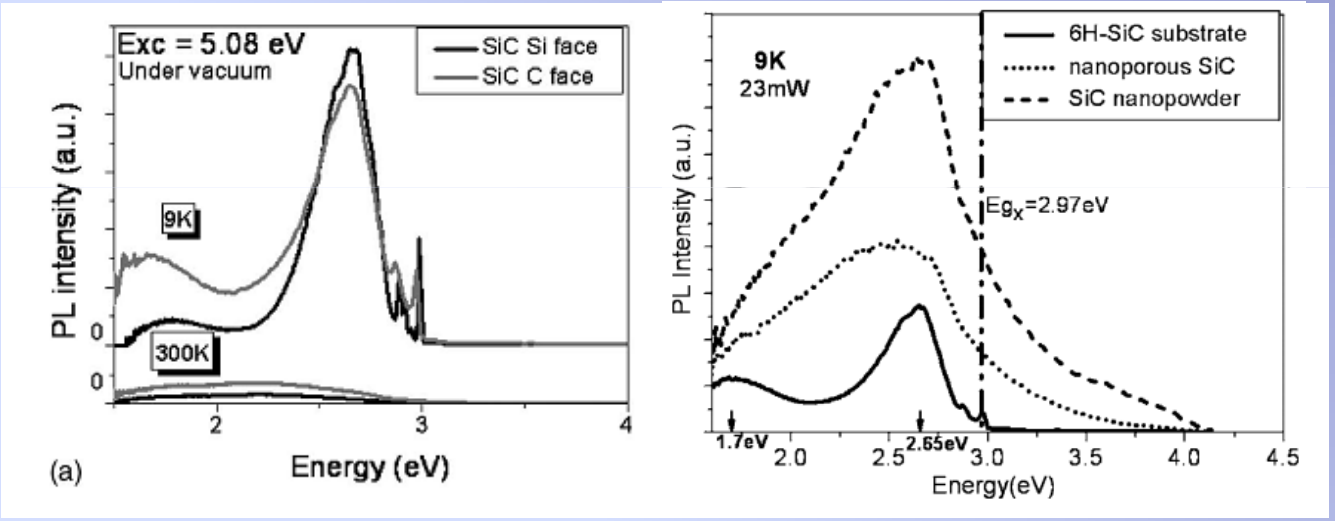
Outline

- ✓ **Cluster approach for SiC electronic and vibration properties modeling**
  - Motivation
  - Hierarchic computational approach
  - Local field model
- ✓ **TiO_2 electronic properties modeling using cluster approach**
  - Isolated TiO_2 clusters, N doped TiO_2, TiO_2 \dye
- ✓ **Electronic properties modeling of $BiVO_4$**
- ✓ **Summary/perspectives**



Scanning electron micrographs of MgB_2/SiC metamaterial
[*N. Limberopoulos et al. Appl. Phys. Lett. 95, 023306 (2009)*]

Silicon carbide is one of the most promising semiconductor materials for high power electronics as well as one of the best biocompatible materials due to its superior properties.

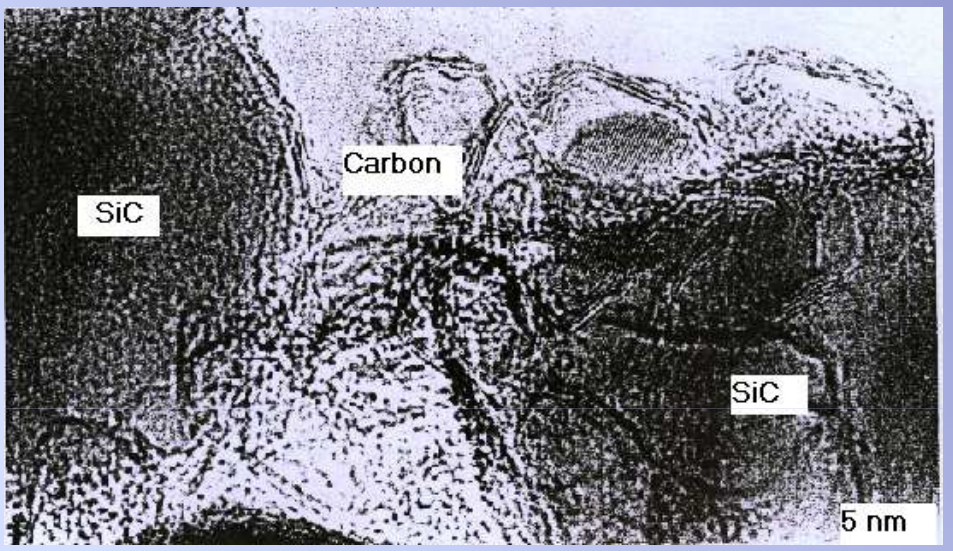


a) PL spectra taken on both sides of the crystalline 6H–SiC wafer at 9 and 300 K. b) Low temperature PL spectra of SiC wafer(C side), nanoporous SiC, and SiC nanopowder. [Botsoa et al. J. Appl. Phys.102, 083526 (2007)]

Silicon Carbide nanoparticles

Investigated SiC nanoparticles have different:

- **Structure** — 3C – SiC, 6H - SiC
- **Size** — 10 – 50 nm
- **C/Si ratio** — C/Si 1.10 – 0.85



A high-resolution TEM image evidences the covering of the particle surface by carbon sheets

A. Kassiba, M. Makowska-Janusik, J. Boucle, J.F. Bardeau, A. Bulou, N. Herlin, M. Mayne, X. Arman, *Diamond and Related Materials 11 (2002) 1243–1247*

Model of SiC nanograins

Cluster model

✓**Clusters possessing about 200 atoms**

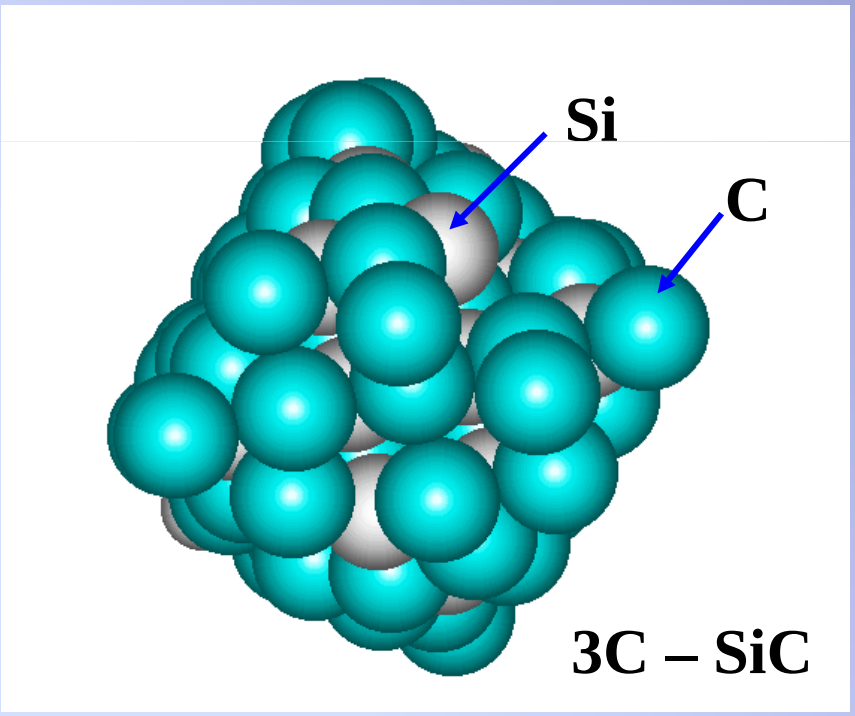
✓ **Clusters covered with carbon**

Simulated structures

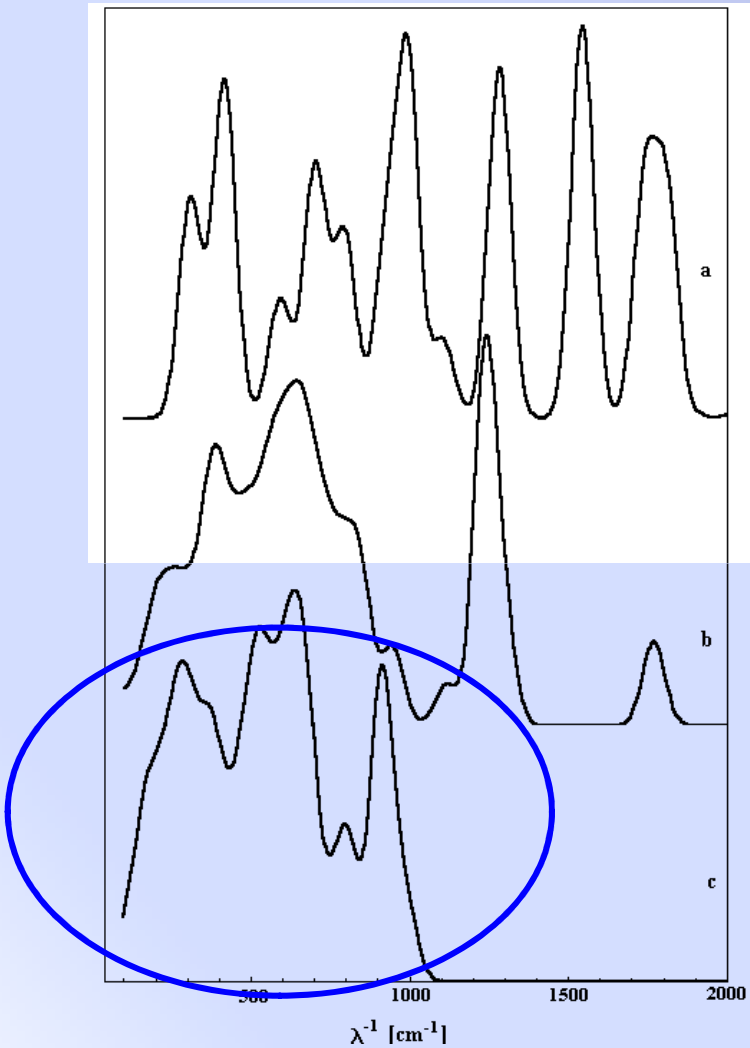
✓**3C-SiC and 6H-SiC ideal structures**

✓**Partially reconstructed structure**

✓ **Amorphous structure of SiC**

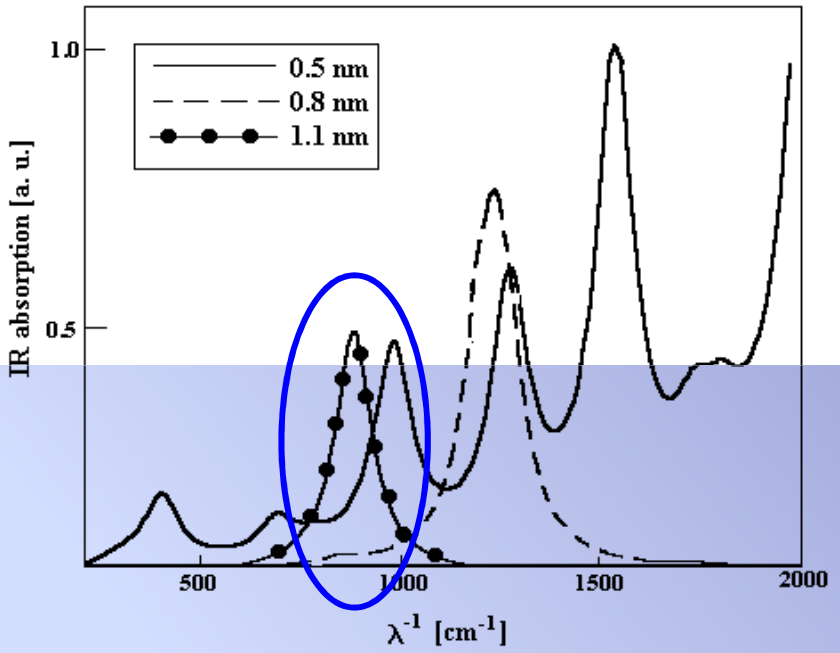


Test of cluster size



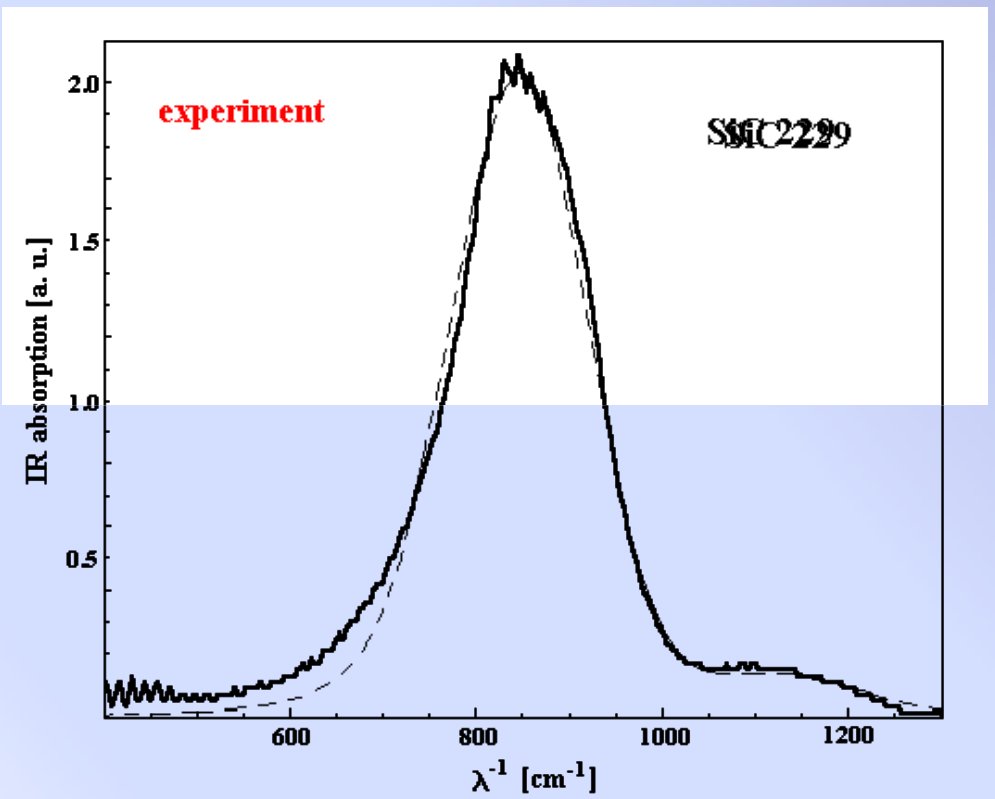
Phonon DOS for 3C-SiC nano-clusters : 0.5 nm (a), 0.8 nm (b), 1.1 nm (c).

IR absorption spectra for 3C-SiC nanoclusters: 0.5 nm (a), 0.8 nm (b), 1.1 nm (c).



M. Makowska-Janusik, A. Kassiba, J. Bouclé, J-F. Bardeau, S. Kodjikian, A. Désert,
***J. Phys.: Condens. Matter*, 33 (2005) 5101**

IR absorption spectra for SiC nanoclusters



- *SiC amorphous structure*
- *β-SiC defected structure*

M. Makowska-Janusik, A. Kassiba, J. Bouclé, J-F. Bardeau, S. Kodjikian, A. Désert,
***J. Phys.: Condens. Matter*, 33 (2005) 5101**

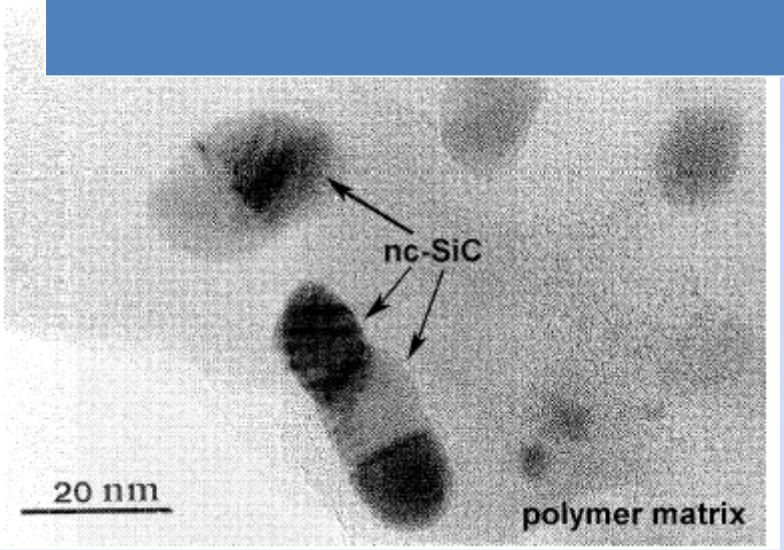
Characteristic of the host-guest silicone carbide based materials

✓ **In the investigated host-guest system the SiC nanoparticles are embedded into polymeric matrix (not grafted)**

Requirements:

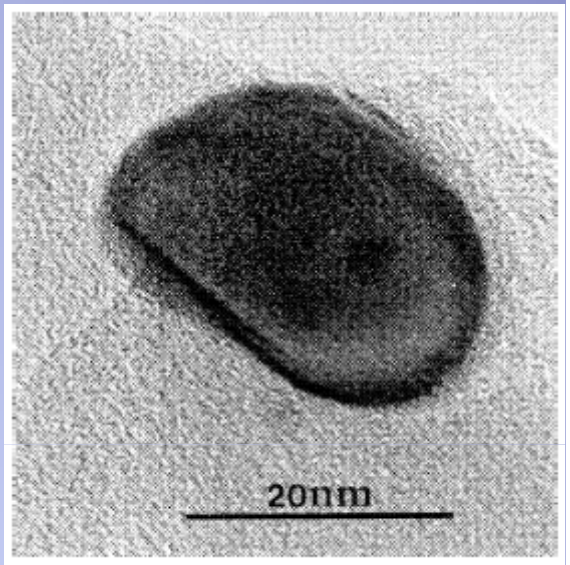
- **The wt % of SiC nanoparticles should be appropriate in order to not agglomerate (3 – 6 wt %)**
- **Dissolution of small molecules in host material decreases its T_g. There should be chosen polymers with relatively high T_g and well transparent for light used in experyment**

Characteristic of the host-guest silicone carbide based materials

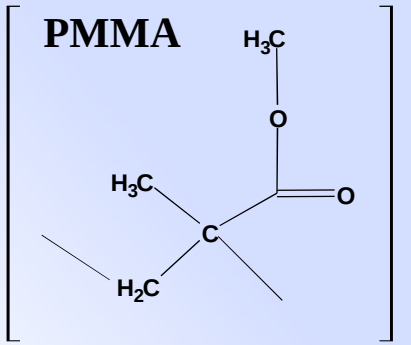


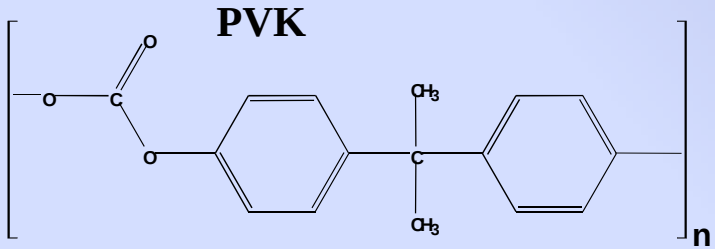
SiC where incor-porated into polymeric matrix:

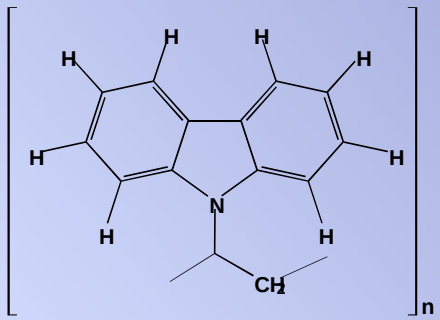
- **PMMA**
- **PVK**
- **PC**



TEM image of the composite PVK/ SiC system.
It shows the local dispersion of the nc-SiC in the polymer matrix.





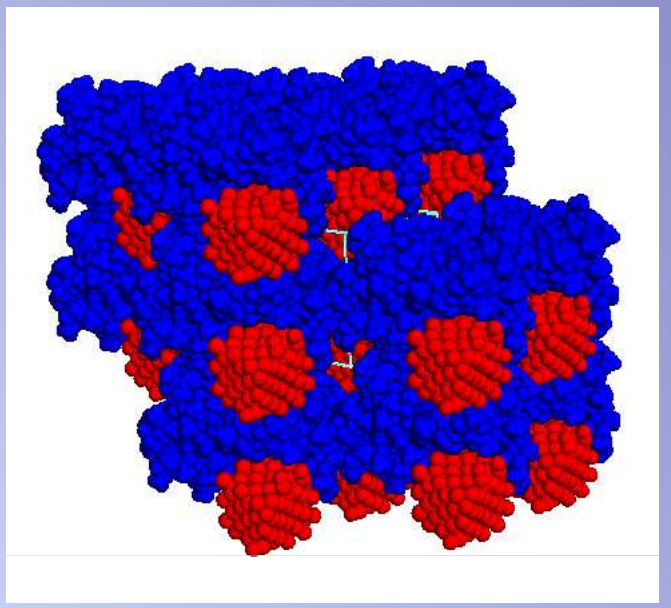


J. Bouclé, A. Kassibaa,J. Emerya, I.V. Kityk, M. Makowska-Janusik, J. Sanetra, N. Herlin-Boime, M. Mayne, *Physics Letters A 302 (2002) 196–202*

Bulk system approach

Requirements:

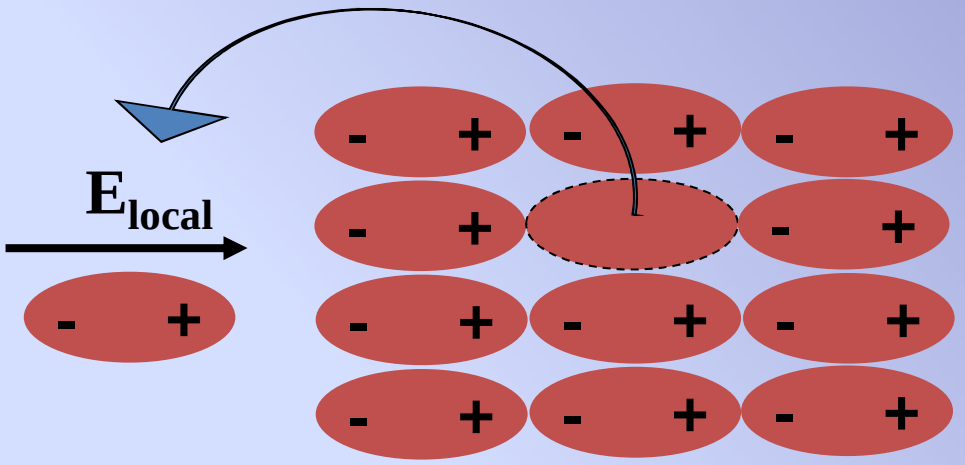
- **SiC cluster should be separated one from the other (Drude nonpolar fluid model)**
- **Cluster should be big enough to model influence of polymer on structural properties of dopant**
- **The size of SiC cluster should allow the quantum – chemical calculations of optical**



Local field

$$E_{loc} = E_{ex} + E_{el} + E_{d}$$

Calculated by removing molecule and evaluating field at the point of interest from neighbour charges and dipoles surrounding this point.



M. Makowska-Janusik et al., *J. Phys. Chem. B 2004, 108, 588-596;* M. Makowska-Janusik et al., *Theor Chem Acc (2005) 114: 153–158*

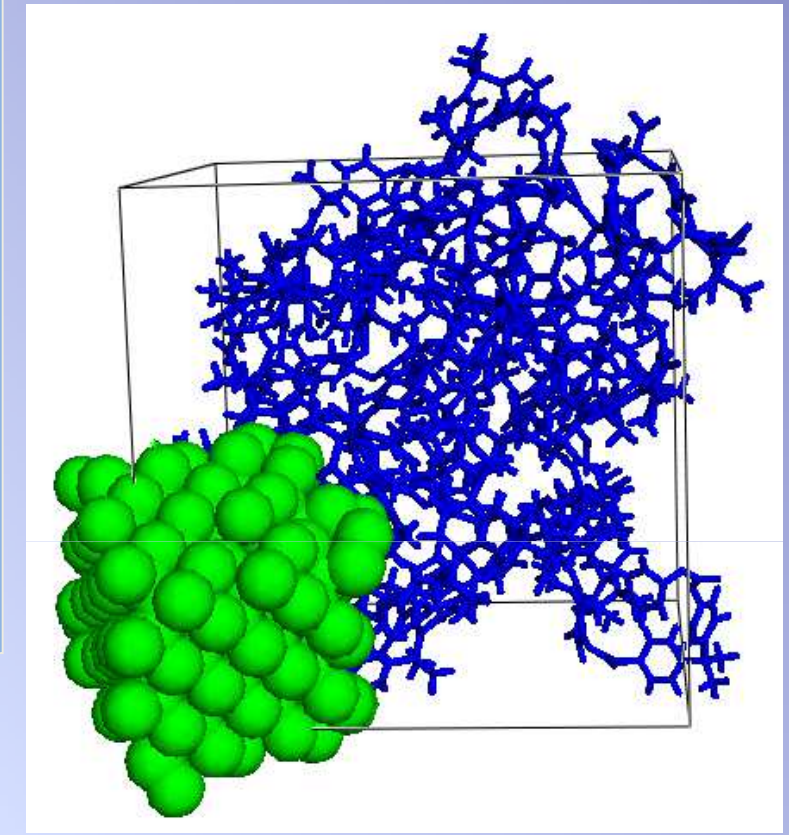
Parameters of molecular dynamics simulations

Density of the simulated systems 1.20 g/cm^3

PMMA 90-mer - molecular wt. 9012.58 amu
PC 50-mer – molecular wt. 12716.21 amu
PVK 50-mer – molecular wt. 9664,45 amu

SiC - 216 atoms - mass 4330.48 amu

PMMA/SiC - 48.05 wt %
PC/SiC - 34.05 wt %
PVK/SiC - 44.81 wt %



MM - molecular mechanics method

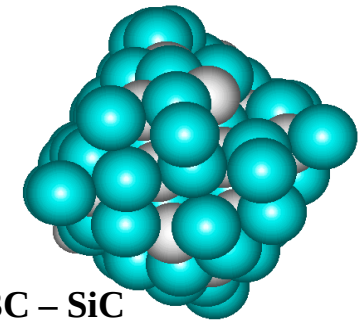
Force field - all-atom consistent valence force field (CVFF)

Boundary condition – 3D Ewald summation

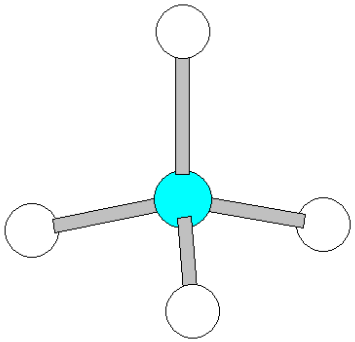
Cutoff – 1.30 nm

GROMACS:
The World's fastest Molecular Dynamics - and it's GPL!

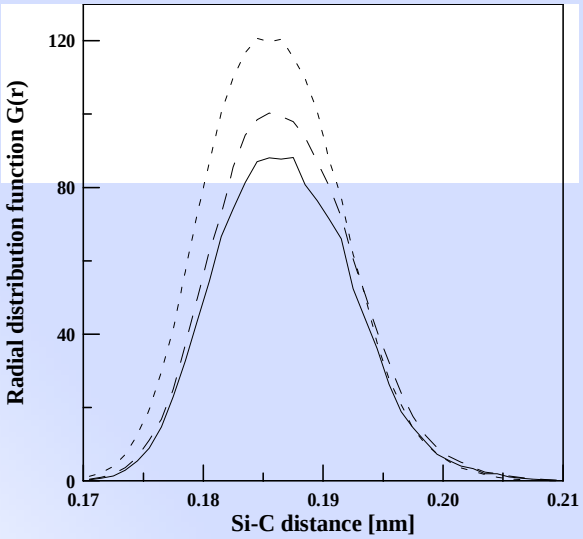
Cluster model



3C – SiC



- ✓ Clusters possessing up to 200 atoms
- ✓ Clusters covered with carbon

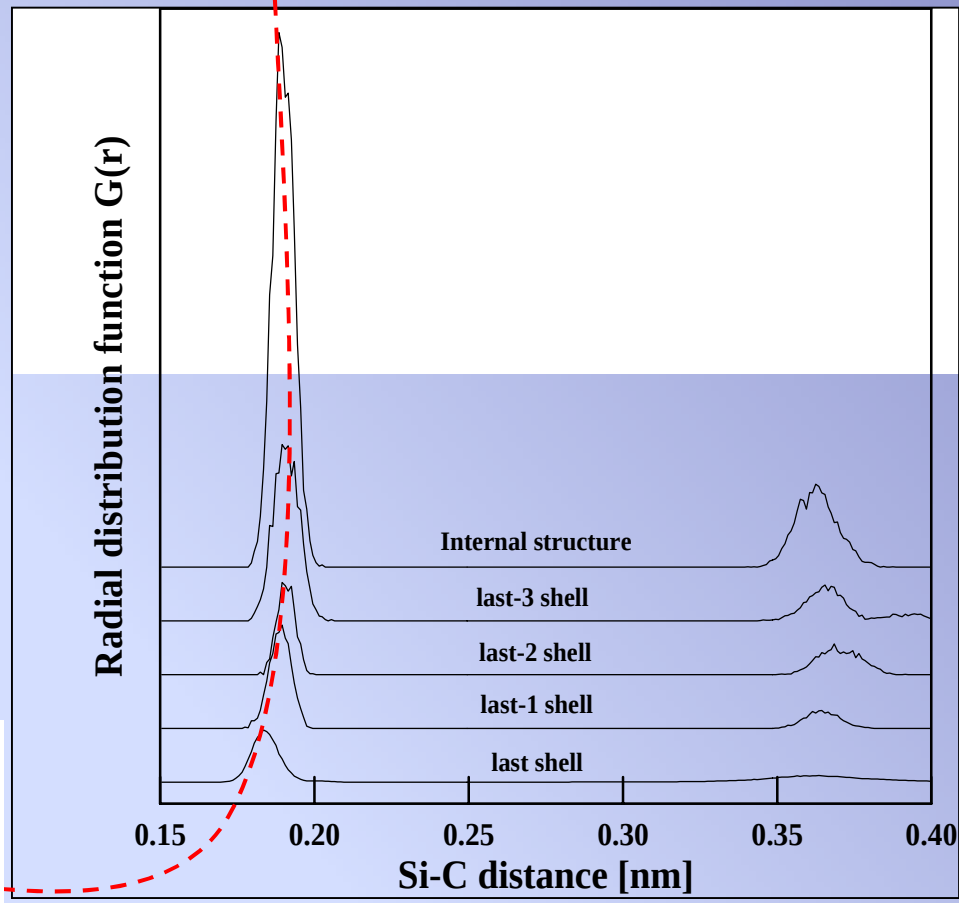


S-C distances

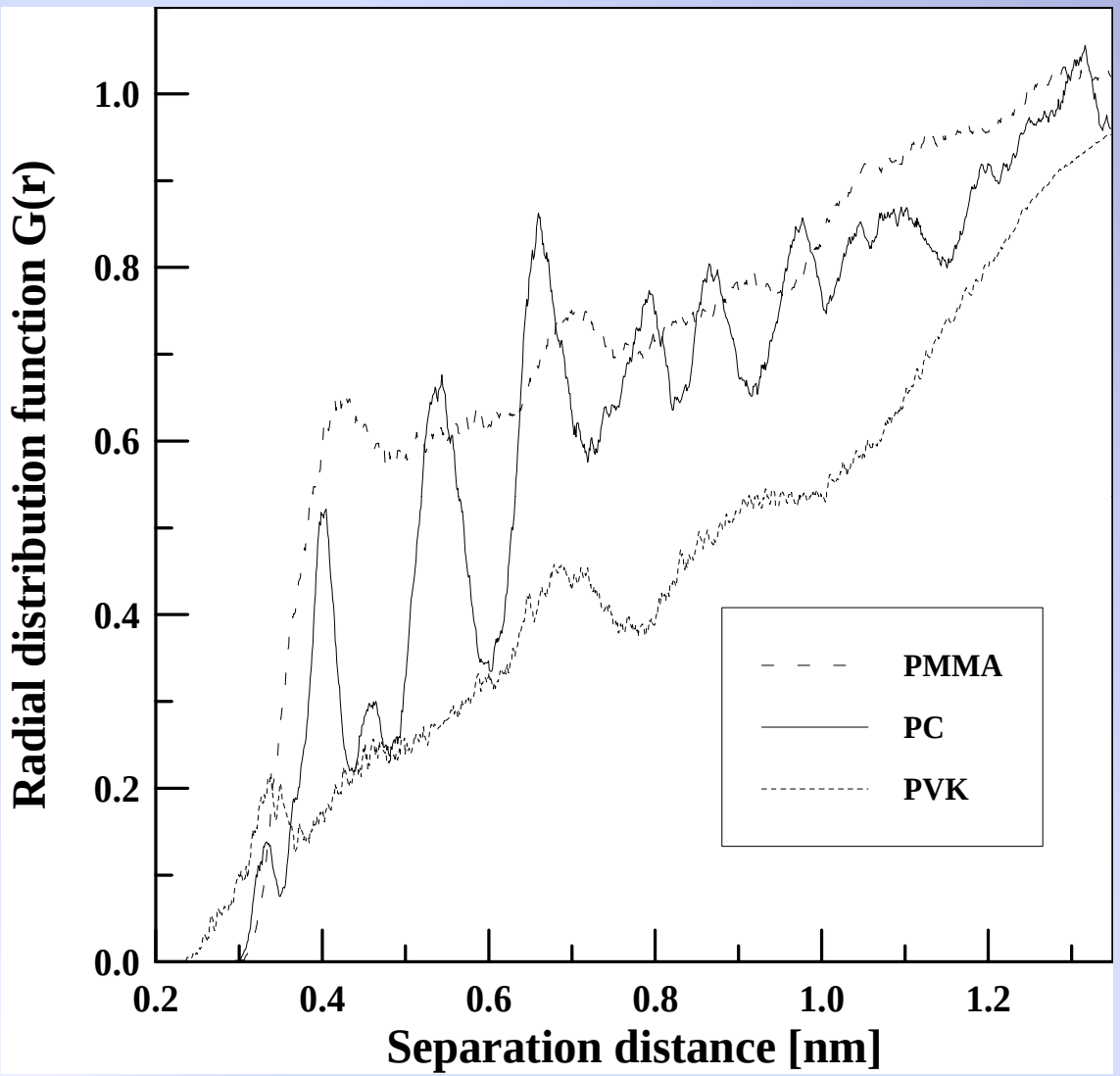
Si-C distance it is intrinsic cluster property

R_1 = 1.88 Å

R_2 = 3.61 Å



SiC – polymer distance



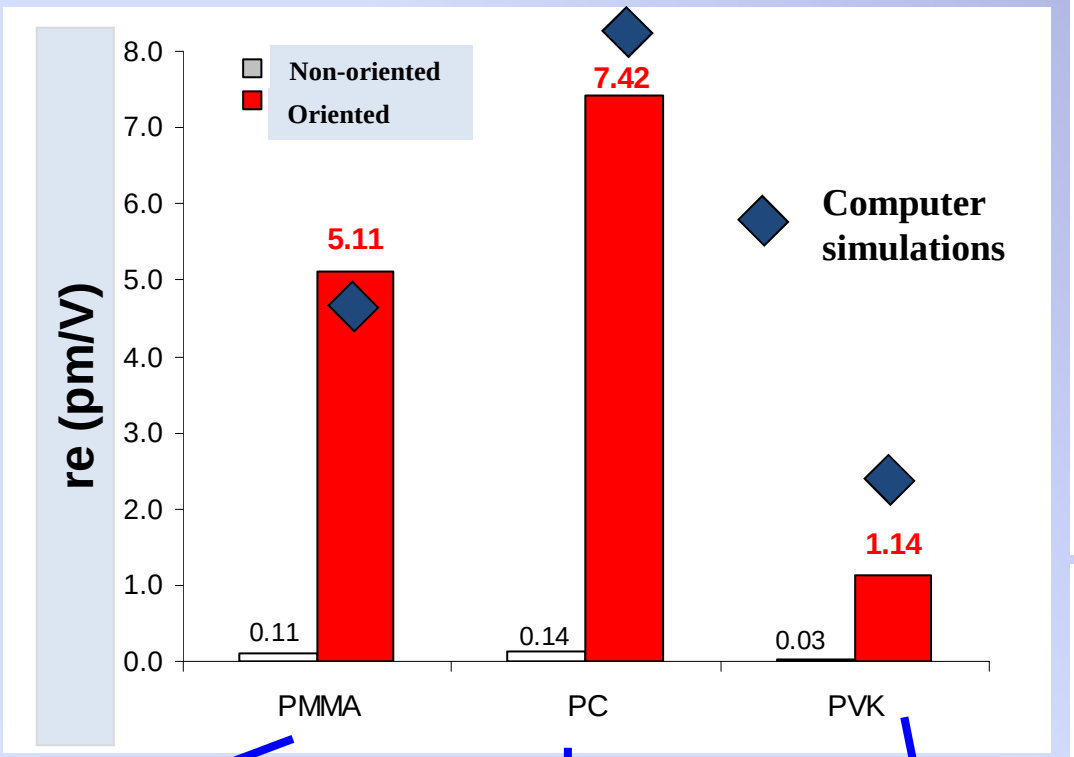
The shortest distance between COM of SiC and polymer's groups

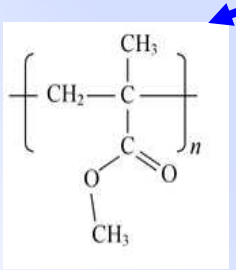
PMMA

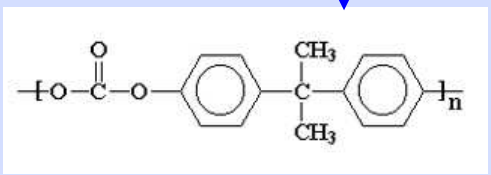
PC

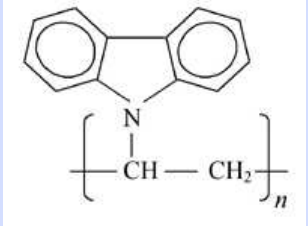
PVK

Electro-optical propertyy of investigated systems



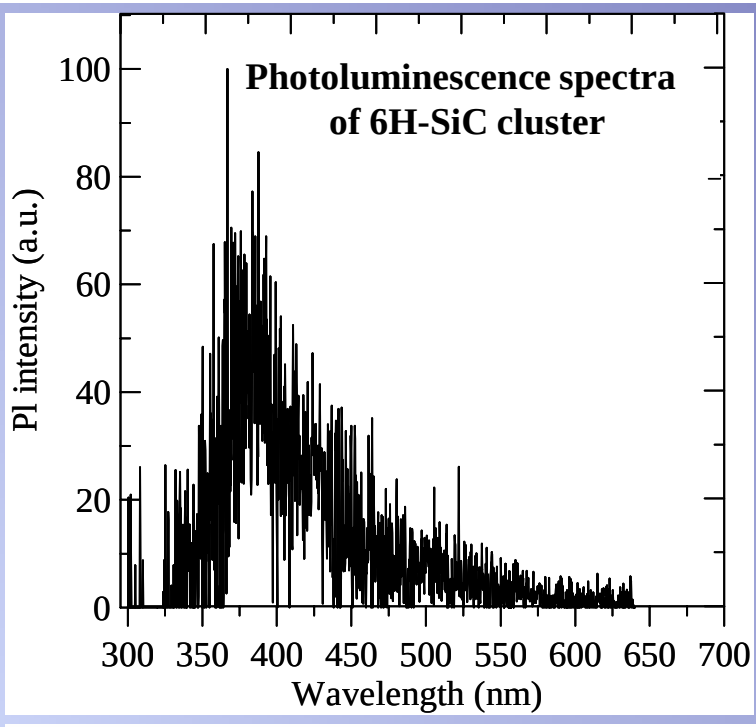


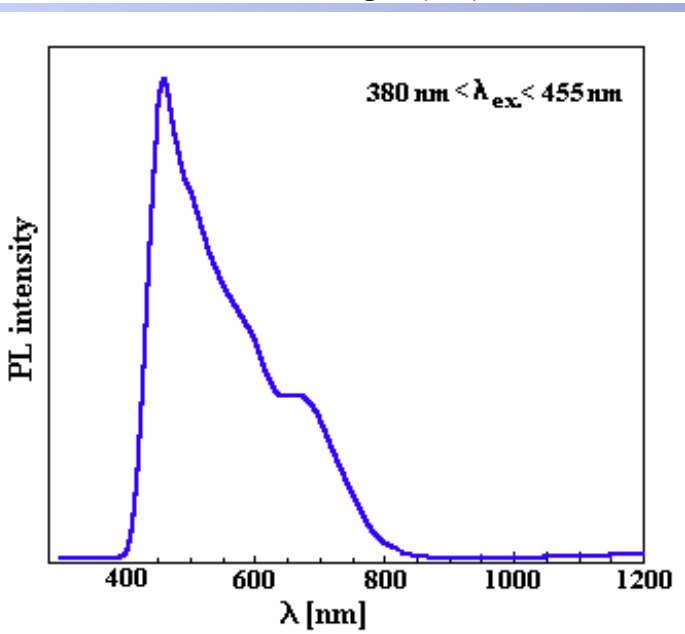




System parameters:

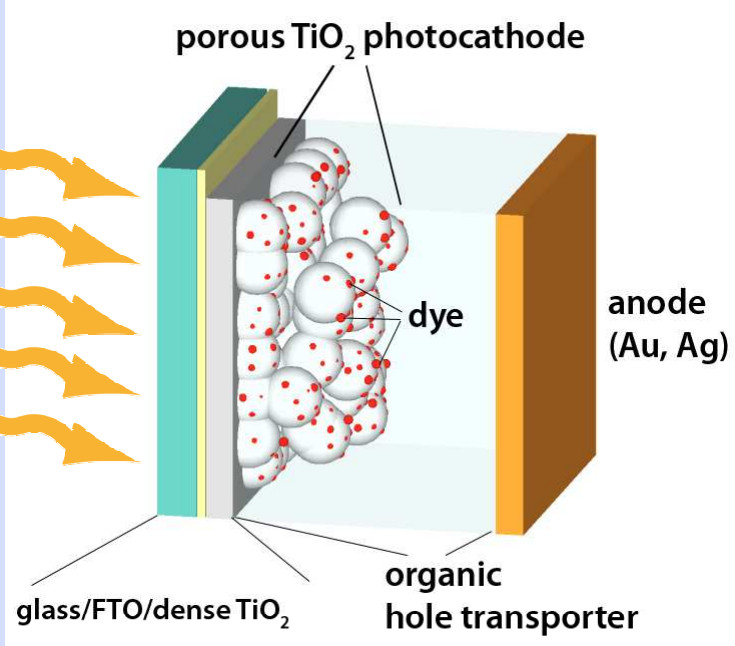
1% SiC 218/1400°C, C/Si<1, d = 39 nm



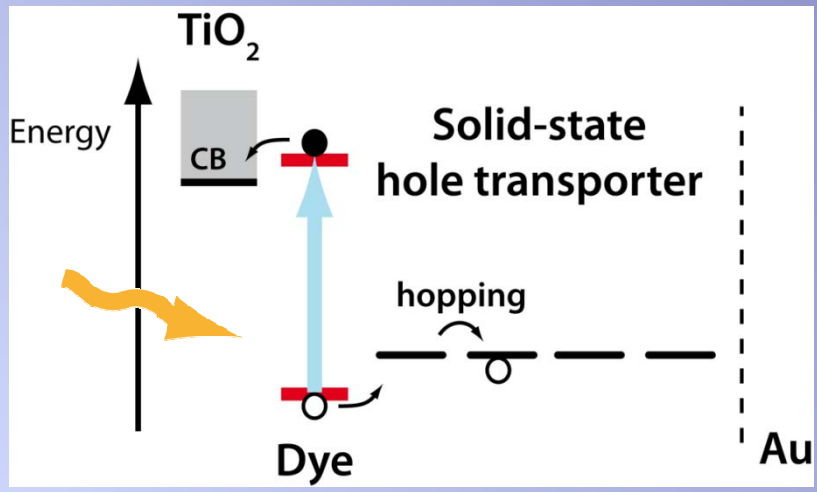


J. Boucle, A. Kassiba, M. Makowska-Janusik, J. Sanetra, N. Herlin-Boime, A. Bulou, S. Kodjikian, Optics Communications 246 (2005) 415–420

Solid-State Dye-Sensitized Solar Cells (DSC)

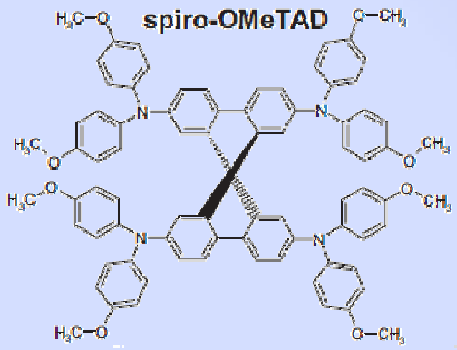


U. Bach, M. Grätzel et al. *Nature* 395 (1998) 583
B.E. Hardin et al. *Nat Photon* 6 (2012) 162-169



Hole conductor - Spiro-OMeTAD

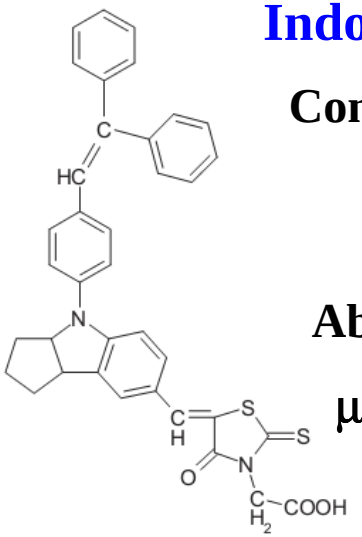
HOMO ~ 5 eV
T_g = 121°C



- ✓ Allows efficient dye regeneration
- ✓ Suitable TiO_2 pore filling up to several mm

J. Krüger et al., *Appl. Phys. Lett.* 79 (2001) 2085
I.-K. Ding et al., *Adv. Funct. Mater.* 19 (2009) 2431

Indoline dye – D102



Conversion efficiency

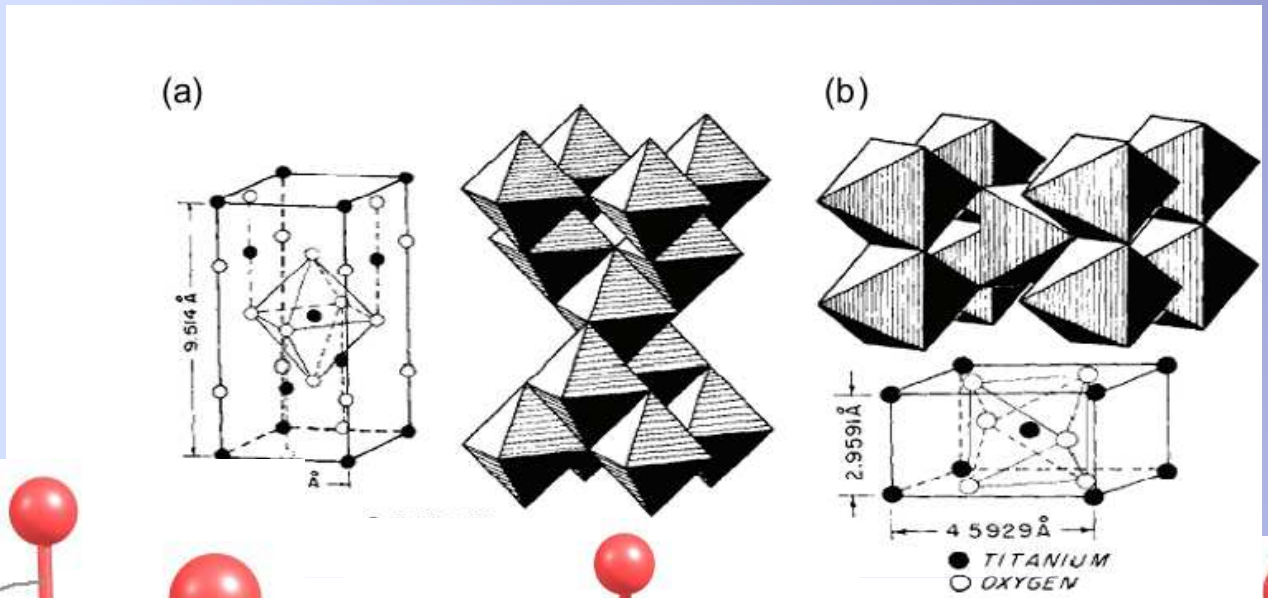
η = 7%

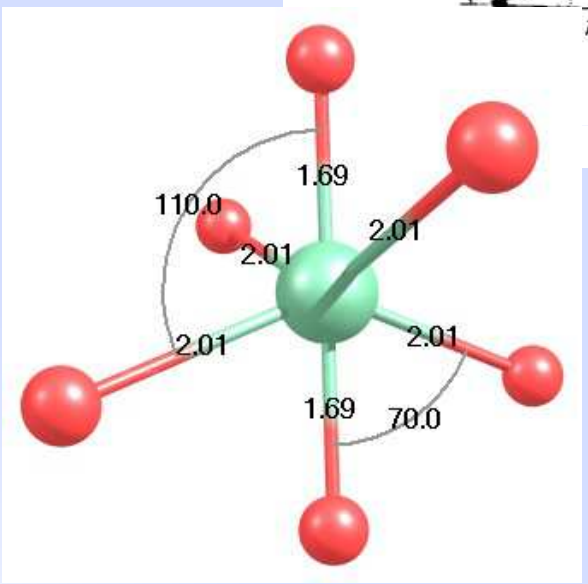
Absorption coefficient

μ=55 800 L $mol^{-1}cm^{-1}$

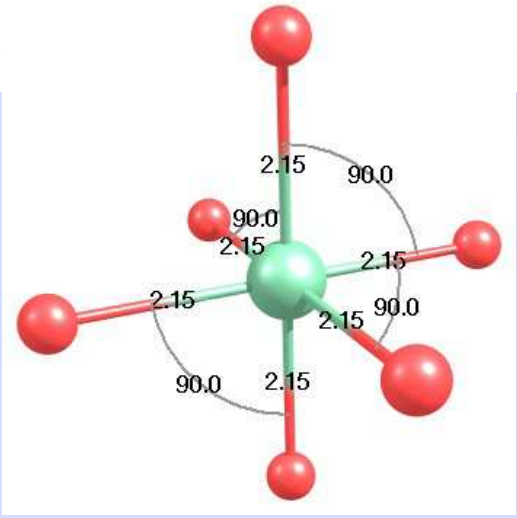
J. Burschka et al., *J. Am. Chem. Soc.* 133 (2011) 18042-18045

Crystal structures of TiO_x

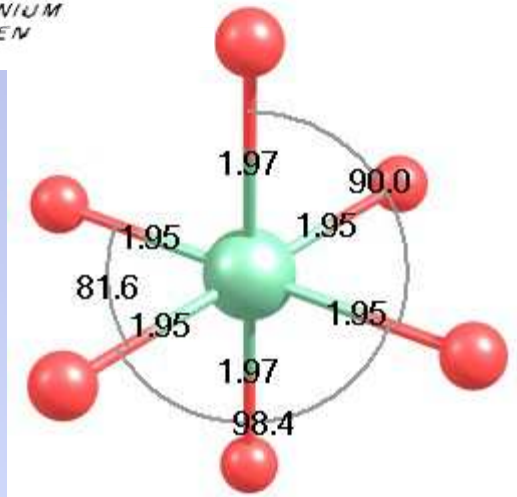




ANATASE



TiO



RUTILE

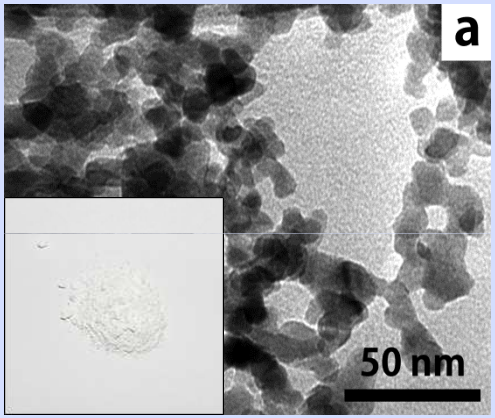
TiO_2 and N-TiO_2 Nanoparticles Synthesis by Laser pyrolysis

B. Pignon et al. *Eur. J. Inorg. Chem.* (2008) 883

Liquid precursor - *Titanium Isopropoxide (+ C_2H_4) (aerosol)*
N-doping : *addition of NH_3*
Production rate - *20g/h (lab. scale)*

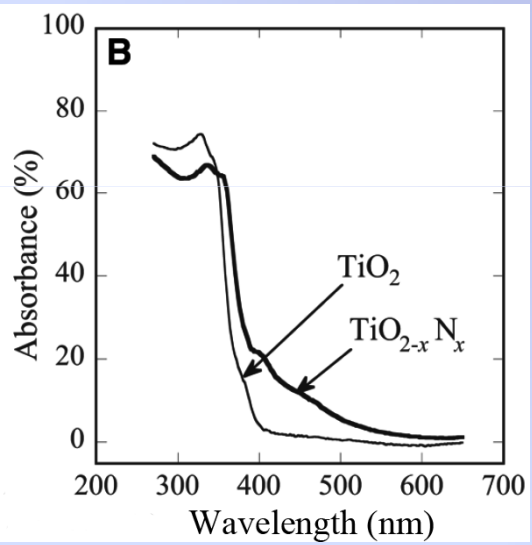
+ soft annealing in air at 400°C (remove C)

TiO_2

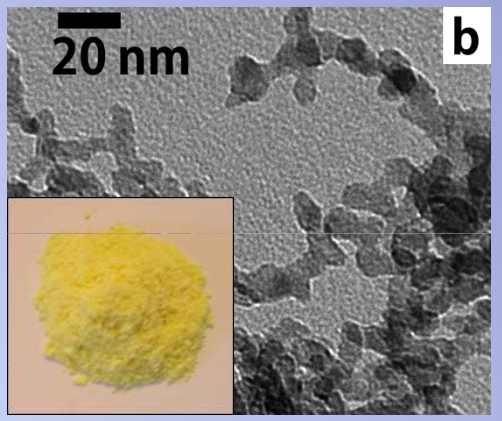


< d > = 12.5 ± 2.5 nm
Anatase > 95 %

Wide band gap material (E_g > 3eV)



N-TiO_2



< d > = 7.5 ± 1.8 nm
Anatase > 95 %
N content = 0.5 at.%

- **Cheap – abondant – non toxic**
- **Leads to best performance up to now**
  > 12% in 2011 with a liquid electrolyte

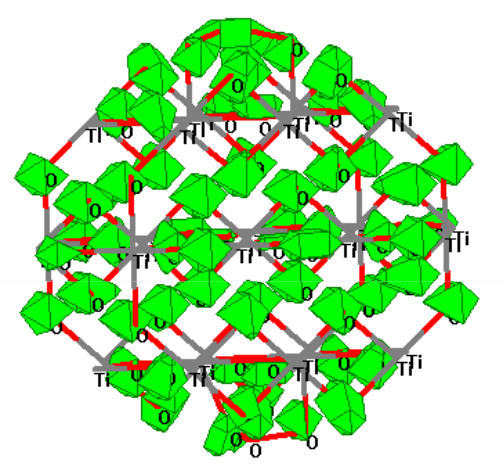
***Doping procedures* ⇒ photo-activity in the visible**

A. Yella et al. *Science* 334 (2011) 629-634

Analysis of the computational method

For the analysis the anathase structure was chosen - It has the simplest and best known structure.

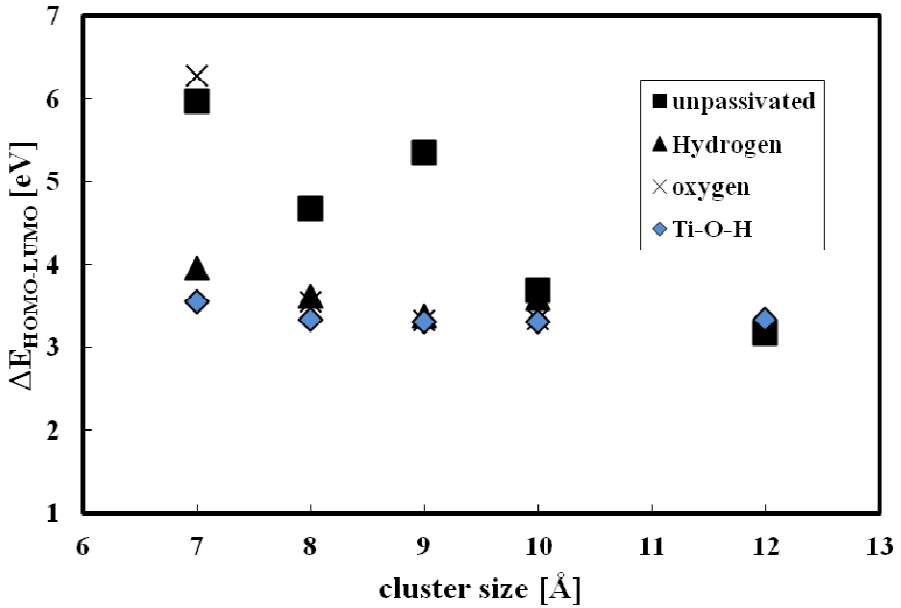
Total charge density redistribution



Semi-empirical PM7

The Ti atoms of rutil are octahedrally coordinated.

The strongly ionic character of the bonds results in localization of charge around the O^{2-} anions



- **The passivation procedure is important for small clusters.**
- **For bigger clusters all passivation methods give the same results**

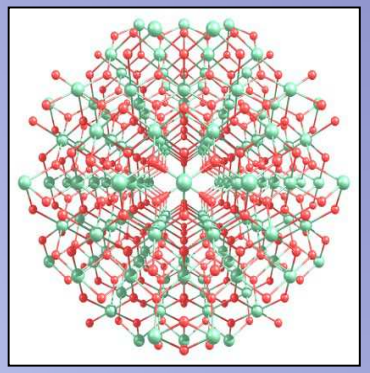
RUTIL
$\Delta E_{HOMO-LUMO}$ **3.06 eV experiment – bulk**
3.17eV PM7 method – cluster 1.2 nm

ANATASE
$\Delta E_{HOMO-LUMO}$ **3.20 eV experiment – bulk**
3.33 eV PM7 method – cluster 1.2 nm
unpassivated

The HOMO-LUMO energy gap splitting of TiO_2 vs cluster siz

DFT methodology with different XC potential

Cluster size [nm]	BLYP	B3LYP	LC-BLYP	CAMB3LYP	LC-BLYP μ=0.8
	$\Delta E_{HOMO-LUMO}$ [eV]				
0.6	0.97	1.04	4.63	2.92	4.76
0.8	0.77	0.83	3.62	2.28	3.97
1.0	0.47	0.50	2.94	1.85	3.03
1.2	0.42	0.45	2.91	1.46	3.03



$$E_X = E_X^{sr} + E_X^{lr}$$

E short range DFT

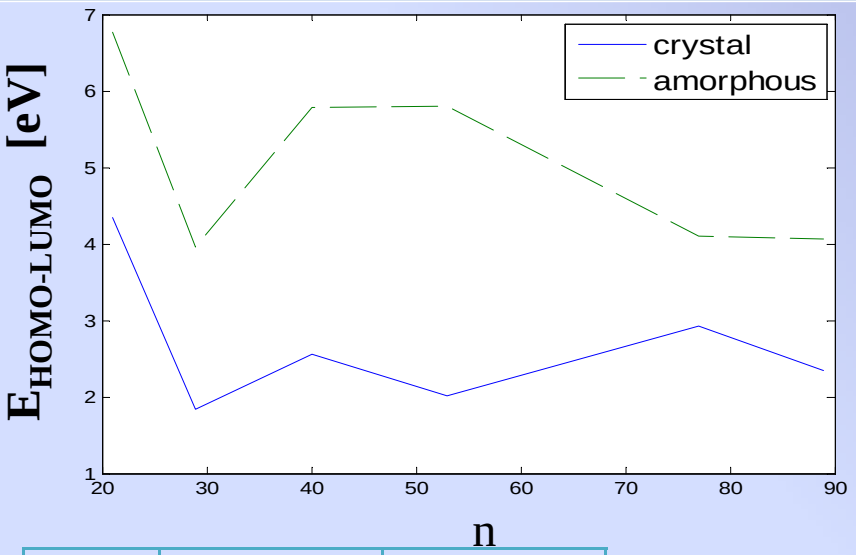
x

$$\frac{1}{r_{12}} = \frac{1-\mathrm{erf}(\mu r_{12})}{r_{12}} + \frac{\mathrm{erf}(\mu r_{12})}{r_{12}},$$

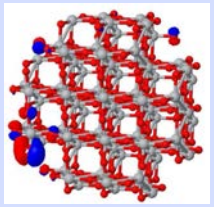
HOMO-LUMO energy gap splitting calculated for unpassivated $(TiO_2)_n$ anatase cluster with diameter equal to 1.0 nm using LC-BLYP functional vs range separation parameter μ

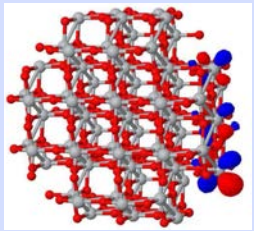
DFT functional	μ=0.1	μ=0.33	μ=0.5	$\mu \geq 0.8$
	ΔHOMO-LUMO [eV]			
LC-BLYP	2.88	2.94	2.99	3.03

$E_{HOMO\ LUMO}$ energy gap spleeting vs $(TiO_2)_n$ size

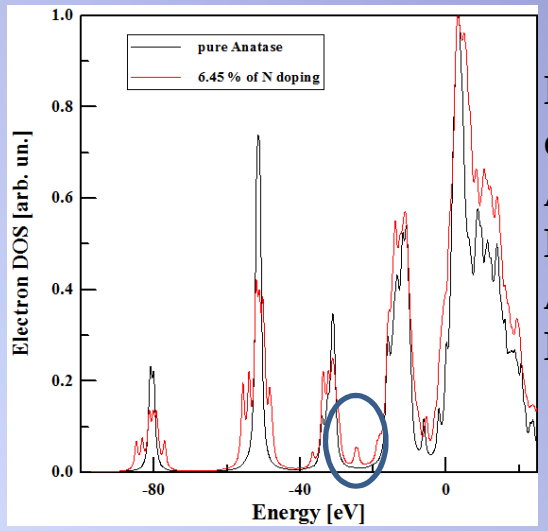


	Crystal	Amorphous
n	HOMO-LUMO	
21	4.343	6.769
29	2.545	5.784
40	1.839	3.951
53	2.004	5.792
77	2.924	4.099
89	2.339	3.058



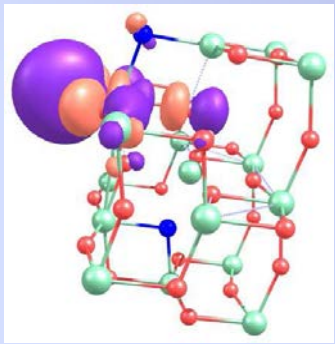


Computer simulation of N-TiO_2 clusters

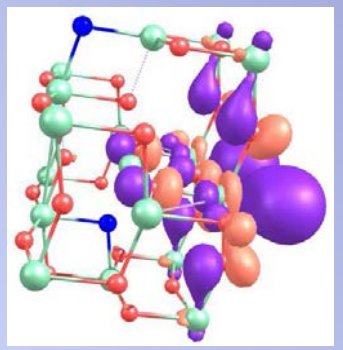


Nitrogen doping – cluster with size 1 nm
Anatase structure
HOMO-LUMO 3.06 eV
Anatase (6.45 % of N)
HOMO-LUMO 2.4 eV

The acceptor character of nitrogen



HOMO

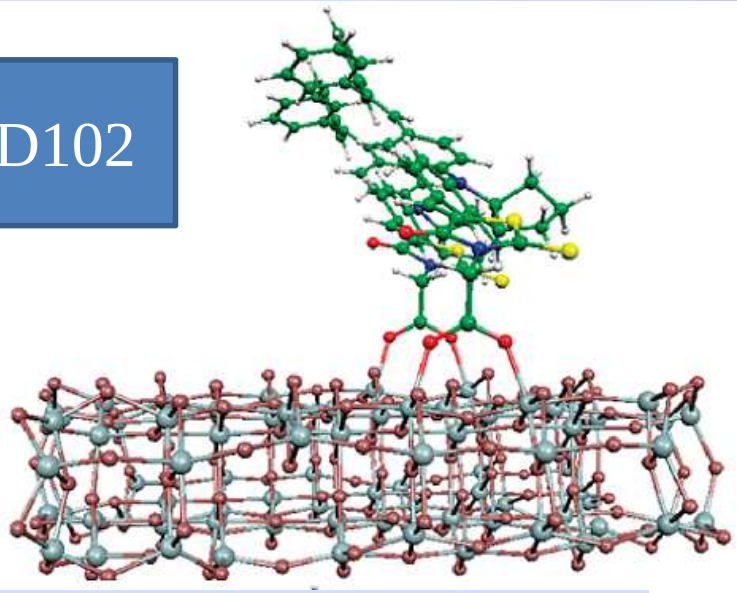


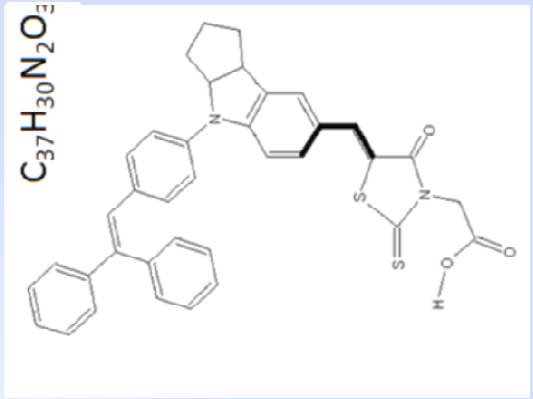
LUMO

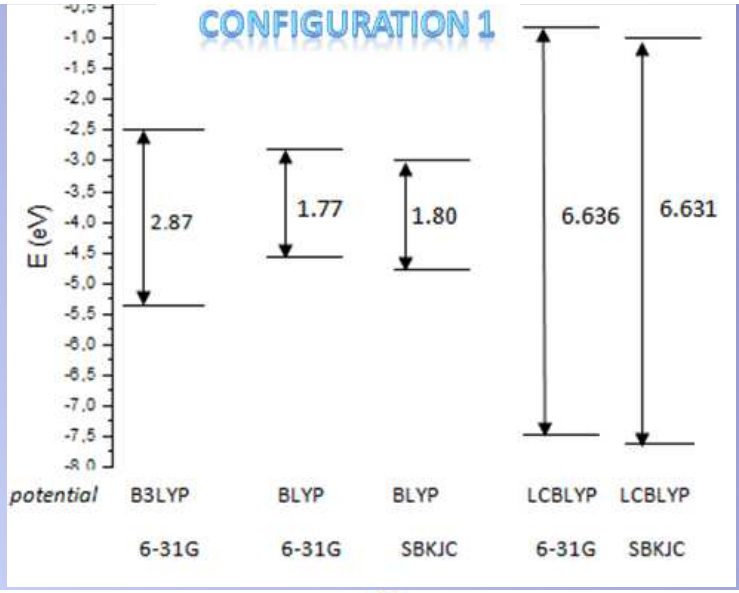
The evidential influence of Nitrogen atomic orbitals on HOMO is seen for the Oxygen vacancy containing clusters

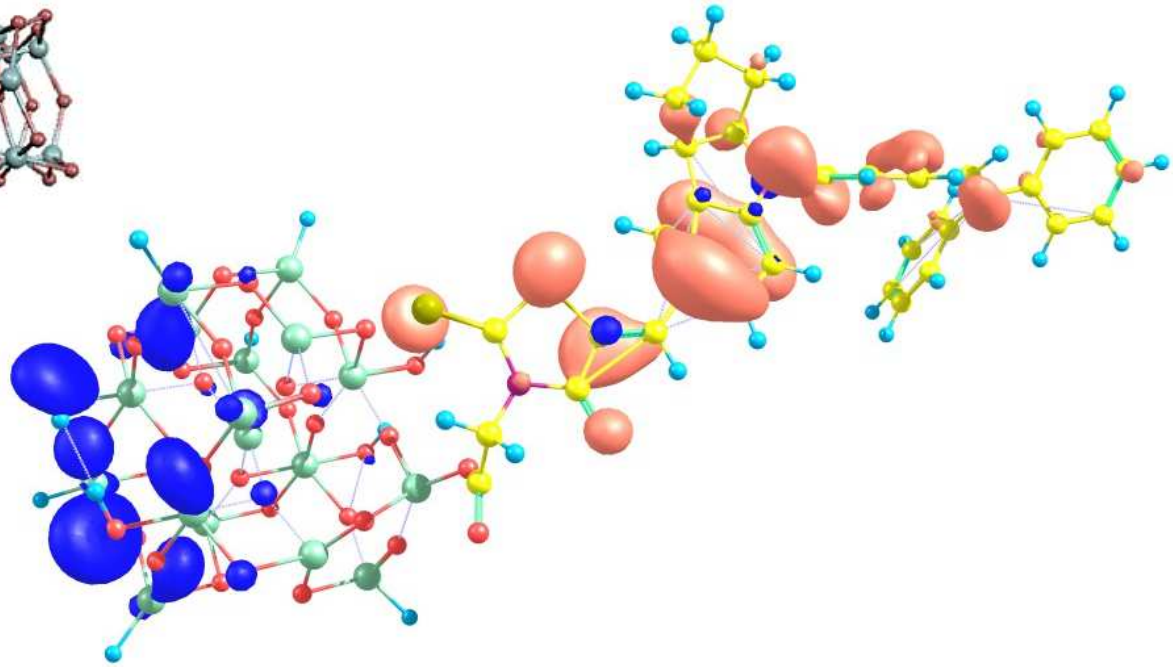
Electronic properties of TiO_2/D102 composite

D102



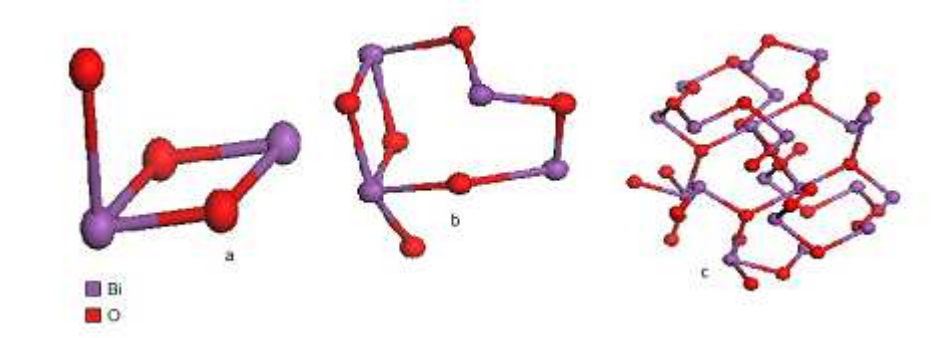






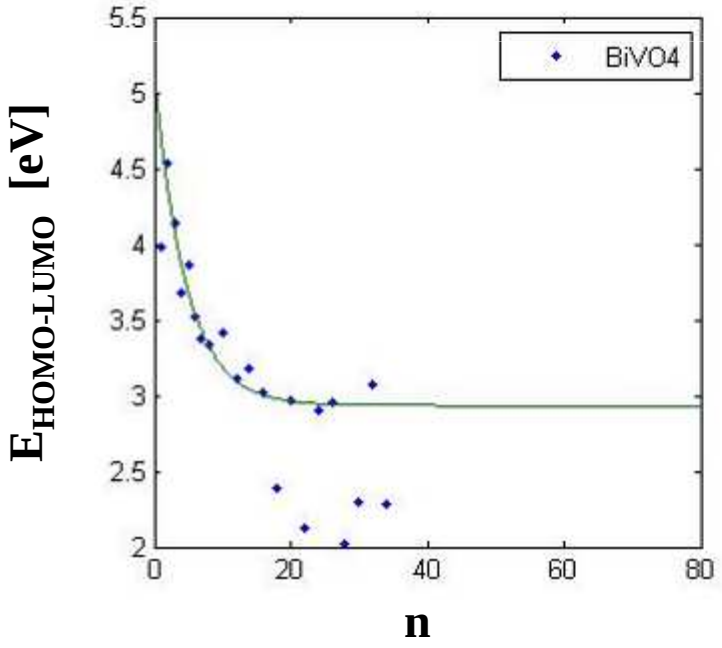
HOMO (red) and LUMO (blue) orbitals redystribution for D102 dye molecule calculated by LC-BLYP functional approximation.

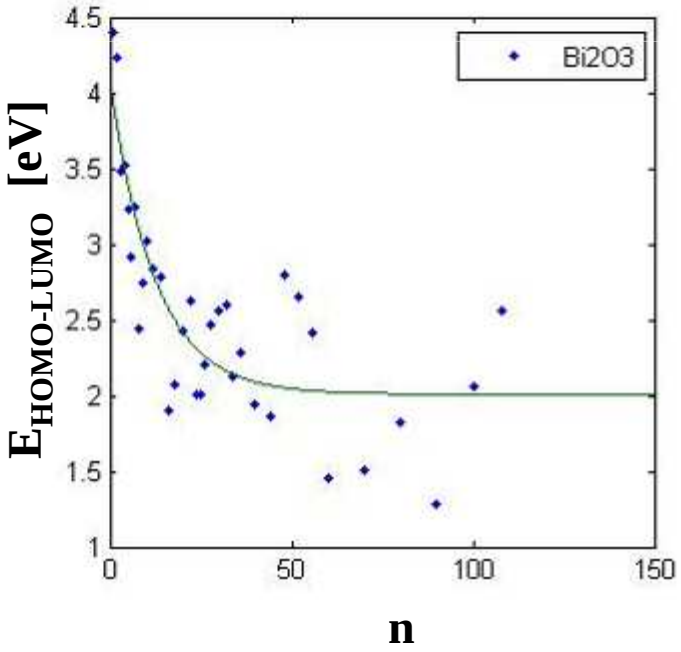
Computer simulations of the Bi_2O_3 and the $BiVO_4$ electronic properties



$BiOV_4$ starting from n=20 has 2.93 eV
Experimental value 2.40 - 2.50 eV

Bi2O3 starting from n=50 has 2,01 eV
Experimental value 2.58 - 2.85 eV





Conclusions

- **Electronic properties of isolated nanoparticles may be calculated using the cluster approach applying the discrete local field approximation**

- **Covalently bounded atoms like SiC or $BiVO_4$ nanoparticles may be calculated using *semi*-empirical or DFT theory.**

- **TiO_2 is the ionic crystal and the LC methodology should be used for the suitable calculations.**

- **The surface passivation and the surface reconstruction is important for the SiC calculations and should be important for all covalently bounded nanostructures .**

- **The TiO_2 as the big nanoparticles may be computer without any defined surface properties.**